Calhoun: The NPS Institutional Archive

DSpace Repository

Theses and Dissertations

1. Thesis and Dissertation Collection, all items

1959

A dilatometer for determining the cubical thermal expansion of solids and applicable for high explosives and propellants.

Briggs, Winston D.

Monterey, California: U.S. Naval Postgraduate School

http://hdl.handle.net/10945/14070

Downloaded from NPS Archive: Calhoun

Calhoun is the Naval Postgraduate School's public access digital repository for research materials and institutional publications created by the NPS community. Calhoun is named for Professor of Mathematics Guy K. Calhoun, NPS's first appointed -- and published -- scholarly author.

Dudley Knox Library / Naval Postgraduate School
411 Dyer Road / 1 University Circle
Monterey, California USA 93943

http://www.nps.edu/library

NPS ARCHIVE
1959
BRIGGS, W.

A DILATOMETER FOR DETERMINING THE CUBICAL THERMAL EXPANSION OF SOLIDS AND APPLICABLE FOR HIGH EXPLOSIVES AND PROPELLANTS

WINSTON D. BRIGGS

LIBRARY
U.S. NAVAL POSTGRADUATE SCHOOL
MONTEREY, CALIFORNIA

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY, CA 93943-5101

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY, CA 93943-5101

UNITED STATES
NAVAL POSTGRADUATE SCHOOL

THESIS

A DILATOMETER FOR DETERMINING
THE CUBICAL THERMAL EXPANSION OF SOLIDS
AND
APPLICABLE FOR HIGH EXPLOSIVES AND PROPELLANTS

* * * * *

WINSTON D. BRIGGS

12ND P2238 (1-59)

Library
U. S. Naval Postgraduate School
Monterey, California

A DILATOMETER FOR DETERMINING
THE CUBICAL THERMAL EXPANSION OF SOLIDS
AND
APPLICABLE FOR HIGH EXPLOSIVES AND PROPELLANTS

* * * * *

WINSTON D. BRIGGS

A DILATOMETER FOR DETERMINING THE CUBICAL THERMAL EXPANSION OF SOLIDS AND APPLICABLE FOR HIGH EXPLOSIVES AND PROPELLANTS

by

Winston D. Briggs

Lieutenant Commander, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

1959

NPS ARCHIVE
1959
BRIGGS, W.

Thesis
B

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHO
MONTEREY, CA 93943-5101

A DILATOMETER FOR DETERMINING THE CUBICAL THERMAL EXPANSION OF SOLIDS

AND

APPLICABLE FOR HIGH EXPLOSIVES AND PROPELLANTS

by

Winston D. Briggs

This work is accepted as fulfilling
the thesis requirements for the degree of
MASTER OF SCIENCE
IN
CHEMISTRY
from the
United States Naval Postgraduate School

ABSTRACT

The need for a semi-precision dilatometer to determine the coefficient of cubical thermal expansion directly from production-lot samples of solid explosives and propellants has become evident in view of critical dimensions and greater operating-temperature ranges of these materials. The dilatometer is fabricated from glassware and operates on the principle of displacing a volume of mercury in a capillary tube. Operating procedures for the dilatometer are set forth in detail and are applicable to all solids, including high explosives and propellants.

The writer wishes to express his appreciation for the assistance and initial direction given him by Dr. C. D. Lind and personnel of the Explosives Division, U. S. Naval Ordnance Test Station, China Lake, California.

TABLE OF CONTENTS

Section	Title	Page
1.	Introduction	1
2.	Dilatometer Assembly	2
3.	Dilatometer Parameters	5
4.	Sample Parameters and Test Conditions	6
5.	Treatment of Data	7
6.	Results	8
7.	Discussion	12
8.	Bibliography	13
Appendix I -	Formula Derivation	14
Appendix II -	Method of Determining Cross-Sectional Area of Capillary	15
Appendix III-	Treatment of Data	18
Appendix IV -	Operating Instructions	23

LIST OF ILLUSTRATIONS

Figure		Page
1.	Dilatometer Assembly	3
2.	Graph of Temperature-Meniscus Location for Typical Test Samples	9
3.	Variation of Area in Capillary	17
4.	Graph of Temperature-Ln Function for Typical Test Samples	20

TABLE OF SYMBOLS

Symbols:

A	Cross-sectional area of capillary, cm^2
$A(x)$	Cross-sectional area of capillary as a function of x
a	Coefficient of cubical expansion, cm^3/cm^3-°C.
B_o	Estimate of the intercept of the regression line
B	Estimate of the slope of the regression line
dV	A differential change in volume
dx	A differential change in distance x
T	Temperature in degrees Centigrade, °C
V	Volume, cm^3
V_o	Initial volume, of specimen bulb unless otherwise indicated
$V*$	Volume of mercury used in estimating cross-sectional area of capillary
$V(T)$	Volume in capillary as a function of T
$V(x)$	Volume in capillary as a function of x
x	Distance from capillary index mark, cm
$\Delta x/\Delta T$	Change in position of meniscus with a change in T
y	Length of mercury used in estimating cross-sectional area of capillary, cm

Subscripts:

g	glassware
m	mercury
s	sample
i	an individual component of the system

1. Introduction

The basic physical properties of explosives are often overlooked in favor of those relative properties which define their characteristics such as sensitivity and brisance. Among these neglected properties is the coefficient of thermal expansion. This earlier neglect is easy to justify in view of the somewhat limited temperature range under which an explosive was exposed, and the lack of any critical dimensional tolerances. This neglect also is apparent in the early approach to solid propellants; grains were small, loading was not critical and temperature exposures were limited.

With the entrance of the guided missile, the entire picture of the solid explosive and propellant has changed. The propellant has increased in size and its burning characteristics are largely controlled through critical grain configurations. The explosive warhead must withstand temperatures almost to its point of detonation. It becomes apparent that thermal expansion is now a property of some interest; in certain cases it is perhaps a critical factor in ultimate performance. Propellants and explosives have physical properties closely related to plastics; even a plastic such as methyl methacrylate, with a reasonably low coefficient of expansion will show approximately a two percent increase in volume under a 100°C change in temperature. If this effect were increased several times and applied to the propellant grain in the last stage of a space missile, the result might change the grain configuation completely--and its performance. A similar situation in the case of the solid explosive might produce very unpredictable results. The need for more information on thermal expansion should be apparent.

To complicate the picture further, explosives and propellants are developing as mixtures rather than pure compounds; research activities will be handling several formulations at a time to judge their relative performance. Determining one set of physical properties will not suffice; a continuous process of measurement must be in operation to determine the production-lot properties of that particular material.

The proposed dilatometer is one approach to fulfilling these needs. Its size can be varied to accomodate any size of sample; the dilatometer tested had a volume capacity of about 35 cubic centimeters. Its accuracy is estimated to be within five percent and should be capable of improvement by the use of more elaborate measuring devices and by taking more observations. Operating procedures are simple and the apparatus can be adapted for remote observation of high explosives should they be tested at high temperatures.

2. Dilatometer assembly

This dilatometer is an adaptation of an instrument described in ASTM Test D 864-52 [1], "Test for the Coefficient of Cubical Thermal Expansion of Plastics". The primary difference is that the procedure of sealing the bulb directly could not be applied to explosive, or combustible materials.

Fig. 1 shows the assembly of the dilatometer. All glassware is Pyrex brand 7740 or similar borosilicate glass [2], having a linear coefficient of expansion of $32.5 \times 10^{-7}/^{\circ}C$. Use of Vycor brand 7900 with a linear coefficient of $8.0 \times 10^{-7}/^{\circ}C$ would give better results.

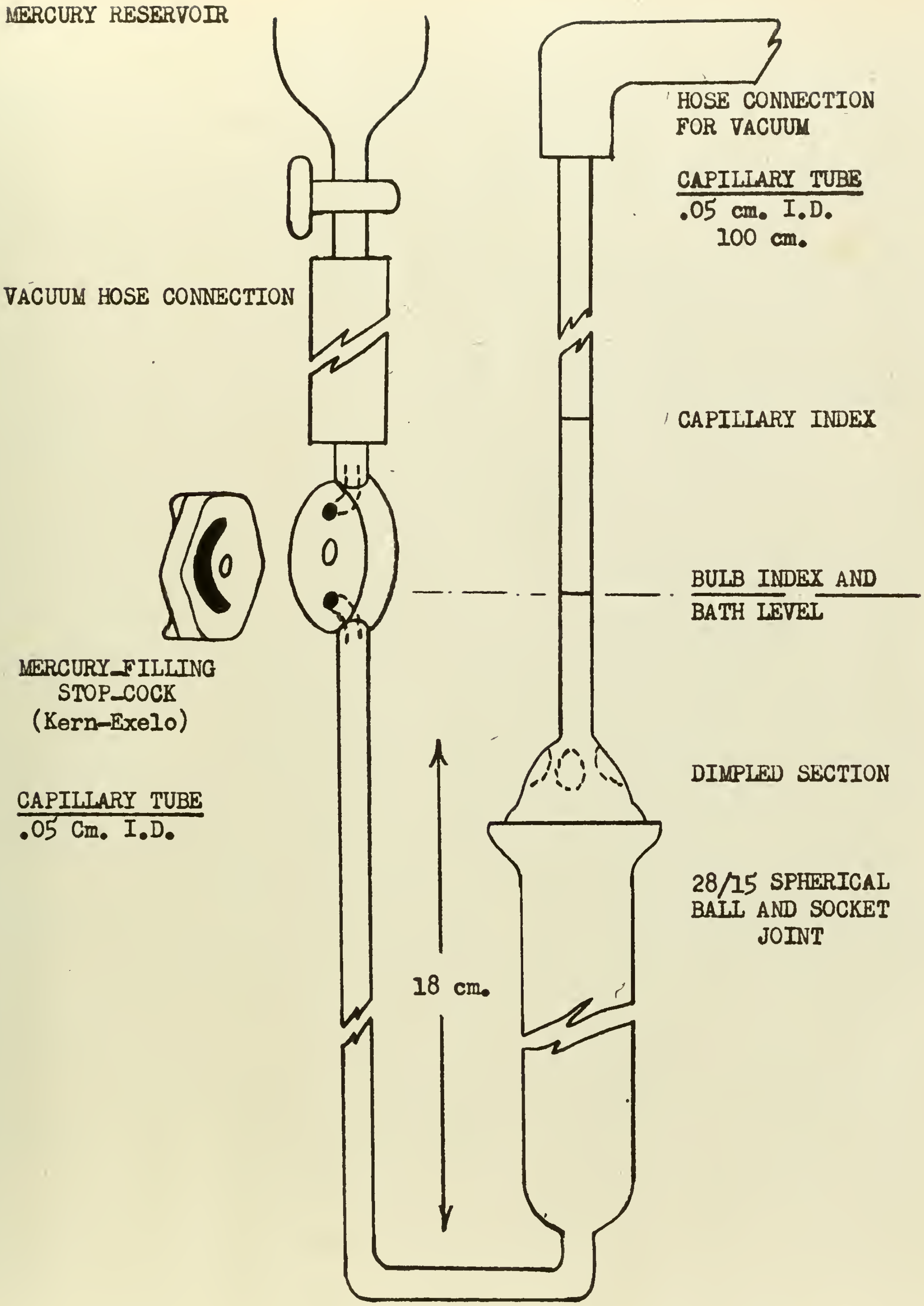

FIGURE 1 — DILATOMETER ASSEMBLY

It should be noted that the specimen bulb is split into two sections and joined by a spherical ball and socket ground glass joint. This joint should be hand-ground carefully with a fine grinding compound to insure a tight and accurate fit. The "dimples" placed in the top section of the specimen bulb are to prevent the sample from blocking the flow of mercury into the capillary section.

The location of the capillary index is arbitrary, as it will be used as the reference position for measurements taken on the capillary. The bulb index mark should be located at the immersion level necessary to cover all glassware which is a part of the closed system.

Two types of stop-cocks were investigated for use on the mercury filling connection. The more satisfactory was a Kern-Exelo type having a flat ground glass surface, requiring no lubricant and safe from being inadvertently loosened. Use of a lubricated stop-cock will result in contamination of the mercury. It is desireable to have a mercury reservoir which is detachable from the dilatometer proper; use of an excess amount of mercury will assist in the initial filling of the system.

A water temperature bath was used with regulation to ± .01 °C. Temperatures were measured to ± .01 °C with a mercury thermometer which had been calibrated with a thermometer certified by the National Bureau of Standards.

Determination of the movement of the mercury meniscus was accomplished with a precision cathetometer, accurate to ± .005 centimeters.

Support for the dilatometer must be fixed with reference to the cathetometer; ease of removal must be considered as well as damping of any vibrations from equipment used in the temperature bath.

3. Dilatometer Parameters

For any individual dilatometer, three parameters must be determined: the volume of the specimen bulb (V_o), the area of the capillary at any point along its length (A), and the effect of the volume of the glassware and its coefficient of expansion (V_g, a_g). Appendix I shows the basic relationships between these parameters.

The volume of the bulb is determined by filling the system to the bulb index with mercury, bringing it to a constant temperature, removing the mercury and determining its weight. Volume can be determined to one part per thousand using a trip-balance.

The cross-sectional area of the capillary is critical in regard to the final results. The approach to this problem will vary with the accuracy desired of the apparatus and the condition of the capillary. Appendix II details the procedures used for these experiments where it was necessary to determine the cross-sectional area with good accuracy.

What is the effect of the coefficient of expansion of the glassware on the system? ASTM Test D 864-52 uses the volume of the specimen bulb as being equal to the volume of the glass, and a value of the coefficient of expansion equal to $1.00 \times 10^{-5}/^{o}C$; these assumptions may lead to error. Owen, White and Smith [3], in their work in determining the density of water, conclude that the coefficient of expansion of glass will have noticeable deviations after fabrication. Therefore, the effect of the volume of the glass and its coefficient of expansion must be determined; this effect, stated in relation to one particular bulb, over a definite temperature range, can be determined by conducting a calibration operation using mercury alone in the system. Procedure for this is

detailed in Appendix III.

One other effect is present but its overall variation on the results would be negligible. This is the change in temperature of the mercury in the capillary and its corresponding effect on the expansion of the mercury and capillary glassware. It is assumed that this would be very small in view of the volumes concerned.

4. Sample Parameters and Test Conditions

Determining a coefficient of expansion for the sample under test will be a cumulative result measured in terms of the initial volume and the change in volume with a change in temperature. It should be realized that the results are in no way a measure of any absolute quantity unless the preceding history of all samples is identical. Due to the nature of the materials being studied, the coefficient of expansion will be in a range of values which are dependent on moisture content, processing method, internal stresses and environment history. Information obtained from the dilatometer will be dependent largely upon the arbitrary test standards established. The primary consideration is that the samples under test arrive at the dilatometer under definite and known conditions.

The samples tested had unknown histories but were subjected to a conditioning period to evaluate this effect on the coefficient of expansion. Other than this, the effect of environment history was not evaluated.

The conditions under which the test is conducted are likewise arbitrary but the following considerations should be observed. A temperature range should be selected which will permit utilization of the

entire capillary; this can be estimated on the basis of the sample size and expected change in volume of the system. The initial temperature so determined will be used in measuring the initial volume of the sample bulb and in evaluating the effect of the expansion of the glassware during the calibration determination. It must be assumed that the coefficient of expansion is essentially constant over this range.

For the tests conducted, a temperature range of 25°C. was selected. This was largely determined by the regulation of the water bath, and sample size was varied to make use of the selected portion of the capillary. The initial temperature was arbitrarily set at 25°C.

5. Treatment of Data

The primary consideration in regard to the data obtained during the testing of the dilatometer was the evaluation of the assembly and procedures rather than any specific coefficient of expansion. Therefore, the methods employed in processing the data were specifically chosen to provide statistical estimates for evaluating overall performance. These procedures are covered in detail in Appendix III and, although tedious to perform, will produce the data necessary for a good statistical analysis. The variation in the cross-sectional area of the capillary can make the processing of data somewhat difficult, however several approaches may be made to this problem. The difference in the final answers will not be significant.

The first method determines the coefficient of expansion in one step by using average values for $\Delta x / \Delta T$ and the area; the average value for $\Delta x / \Delta T$ is computed from individual observations and the average value

for the area is that value which was determined by the procedure outlined in Appendix II. Observations must be made over the entire capillary section which was used in determining the average value of the area. A slight variation in this method is to obtain $\Delta x / \Delta T$ by plotting each observation on coordinate graph paper and determining the slope of the line. This method is illustrated in Fig.2 for typical test data. The second method involves several calculations with an average value being taken as the coefficient of expansion. For each observation the coefficient of expansion is calculated from the $\Delta x / \Delta T$ observed, using the best estimate of the area at the mean location in the capillary over which the expansion occurred.

These methods are satisfactory for determining the coefficient of expansion; for a study of the effects on a particular coefficient under varying conditions, the statistical method outlined in Appendix III will be more reliable.

6. Results

The results, though not conclusive, are sufficiently accurate and reproducible. These are based on the data obtained from testing mercury, Pyrex glassware and methyl methacrylate plastic under conditions which would provide the most useful data, and evaluating these data at a level of significance of five percent. A sufficient number of observations were made in each case to insure that the probability of accepting an erroneous result would be low.

In the determinations conducted with mercury alone in the specimen bulb, the coefficient of expansion was found to be $18.172 \times 10^{-5}/^{\circ}C$,

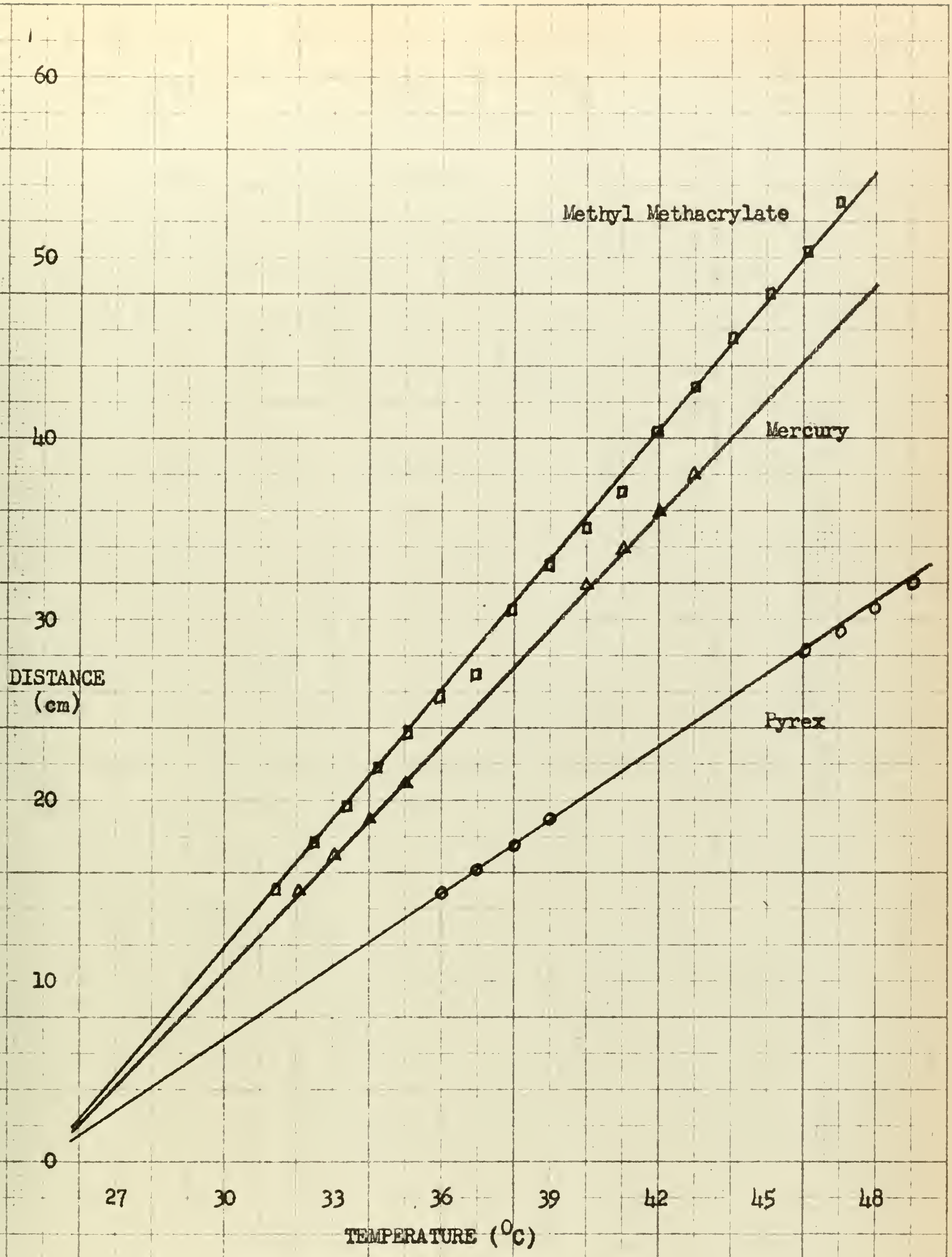

FIGURE 2 — Temperature-Meniscus Location for Typical Test Samples

with a confidence interval of ± .15 x 10^{-5}/°C; the accepted value of the cubical coefficient of expansion [4] is 18.194 x 10^{-5}/°C. The value determined was not significantly different.

The determinations using mercury as a standard established that the expansion of the glassware will not introduce any significant error if the coefficient of expansion of Pyrex is assumed to be 1.00 x 10^{-5}/°C and the effective volume of the glassware is assumed to be that of the specimen bulb.

The reproducibility of the apparatus was established by testing a Pyrex glass rod, since it proved to be the least susceptible to variations in conditioning. On separate determinations a value of .962 x 10^{-5} /°C with a confidence interval of ±.294 x 10^{-5}/°C was found to be in agreement with the derived value of .975 x 10^{-5}/°C, which value is three times the linear coefficient of expansion.[2] However, the significant part of these determinations was that there was no difference in the values determined on separate runs. The large confidence interval is the result of an unfortunate choice of sample size, a factor which was not known at the time of the test.

In later runs, the sample size was varied to study the effect on sample deviation. It would appear that deviation will be approximately proportional to the ratio of the volume of the specimen bulb to the volume of the sample. In assembly of the apparatus, the specimen bulb should be of a size which will just accomodate the sample and its anticipated expansion.

Conditioning of samples will have a marked effect on the results. This was determined from the methyl methacrylate samples using a

constant temperature oven set at 50 °C and varying the time in which each sample was conditioned. One run was started on an un-conditioned sample; the initial expansion was in the order of $30 \times 10^{-5}/^{\circ}C$ and the run was secured when the expansion indicated a sudden decrease of 20%. Samples which were conditioned for 48 hours had a value of $21.600 \times 10^{-5}/^{\circ}C$ and a confidence interval of $\pm .223 \times 10^{-5}/^{\circ}C$; on successive conditioning periods there was a significant decrease. Samples which were conditioned for one week or more had a value of $20.6 \times 10^{-5}/^{\circ}C$ with a confidence interval of $\pm .184 \times 10^{-5}/^{\circ}C$. There was no significant change for successive conditioning periods. Methyl methacrylate molding compound [5] has a specific gravity of 1.17-1.20 g/ml and a linear coefficient of expansion of $5 - 9 \times 10^{-5}/^{\circ}C$; using the usual approximation, this would be a cubical coefficient of $15\text{-}27 \times 10^{-5}/^{\circ}C$. The specific gravity of the samples tested was 1.18 g/ml. On this basis, the values determined are reasonable and of the correct order.

In summary, the test results would tend to indicate that the dilatometer is capable of accurate determinations, within five percent, and good reproducibility provided the sample size is chosen correctly and a conditioning period is used for plastic-like materials. One other aspect was developed as a result of the tests; this concerns the optimum number of observations. Since this is pertinent to specific data treatment, it has been included separately in Appendix III:

7. Discussion

The equipment as assembled and operated with corresponding data treatment will satisfactorily fulfill the original concept of the dilatometer. There are however certain aspects which should be pursued more extensively.

The first of these would be a study of the variation of the expansion of the glassware in regard to time. Once a determination has been made to an elevated temperature, how long must the equipment be permitted to rest before it will return to the original dimensions? One important feature may be the rate of change of temperature. This was brought out during the course of the experiments. One sample was subjected to a gradual temperature increase over a period of 12 hours. On completion the equipment was permitted to cool to room temperature. The following day the temperature bath was heated to the previous temperature at its maximum rate. Upon reaching that temperature, the position of the meniscus was three centimeters higher, and it remained thus for 24 hours. No attempt was made to evaluate this effect, but it was taken into consideration during later determinations in that all runs were uninterrupted by cooling intervals and all temperature changes were in gradual steps.

One uncompleted objective was the determination of "growth" tendencies in plastic materials. The actual determination of the volume of the specimens lacked sufficient accuracy to reveal any detectable changes, but a volume change of approximately 3.0×10^{-5} cm^3 can be detected in the capillary using the equipment described. Provided the previous effect can be evaluated, this suggests that the dilatometer would be suitable

for a study of "growth" tendencies under cyclic environment changes.

8. Bibliography

1. ASTM Standards, Part 6, pp 268-71, American Society for Testing Materials, Philadelphia, Pa., 1955

2. Corning Glass Works, Pyrex Laboratory Glassware, publication LG-1, Corning, New York, 1958

3. Benton B. Owen, James R. White and James S. Smith, *Journal American Chemical Society*, Vol. 78, pp 3561-4, August 1956, "An Evaluation of the Density of Water at 5° Intervals between 45 and 85°".

4. National Research Council, "International Critical Tables", McGraw-Hill Book Co., Inc., New York and London, 1926

5. *Modern Plastics*, Vol. 36, No. 1A, pp 590, September 1958, "Plastic Properties Chart".

6. Albert H. Bowker and Gerald J. Lieberman, Handbook of Industrial Statistics, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1955

APPENDIX I

FORMULA DERIVATION

The change in volume of the system is equal to the sum of the change in each of the individual components,

$$A\,\Delta x = \sum V_i\, a_i\, \Delta T$$

$$A\,\Delta x/\Delta T = V_m\, a_m + V_s\, a_s - V_g\, a_g\ .$$

Rearranging,

$$a_s = \frac{A\,\Delta x}{V_s \Delta T} - \frac{V_m}{V_s} a_m + \frac{V_g}{V_s} a_g$$

$$= \frac{A\,\Delta x}{V_s \Delta T} - \frac{V_m a_m - V_g a_g}{V_s}$$

Where,

$$V_o = V_m + V_s \text{ , } V_m = V_o - V_s$$

$$a_s = \frac{A\,\Delta x}{V_s \Delta T} - \frac{(V_o - V_s) a_m - V_o a_g}{V_s}$$

And assuming that,

$$a_s = \frac{A\,\Delta x}{V_s \Delta T} - \frac{V_o}{V_s}(a_m - a_g) + \frac{V_s}{V_s} a_m$$

$$V_o = V_g$$

$$a_s =$$

Then,

$$a_s = \frac{A\,\Delta x}{V_s \Delta T} - \frac{V_o}{V_s}(a_m - a_g) + a_m$$

APPENDIX II

METHOD OF DETERMINING CROSS-SECTIONAL AREA OF CAPILLARY

In addition to normal variations in cross-sectional area along the length of the capillary, it will be found that there is a severe distortion in the immediate vicinity of the bulb.

The determination of the area was accomplished in the following manner. Approximately five to ten milligrams of mercury was placed in the capillary by inverting the dilatometer and connecting a vacuum line to the mercury-filling connection. A two-foot length of vacuum hose was connected to the capillary stem and closed off; the vacuum was then removed from the system. By compressing and releasing the vacuum hose it is possible to move the mercury to any position in the capillary.

The mercury was then moved in increments of one-half its length throughout the length of the capillary, using the cathetometer to determine the position of the mercury in reference to the capillary index mark. The procedure was accomplished at room temperature and the variation in temperature was not sufficient to affect the density of the mercury.

The data were converted to "length-of-mercury" and its mean location in the capillary. These data were plotted and inspection of the graph indicated those portions of the capillary which were unsuitable for accurate determinations. The section of the capillary between 12.5 and 62.5 cm was judged to be satisfactory, in that it closely approximated a linear relationship with the "length-of-mercury".

A second determination was accomplished over this selected portion; the mercury was removed on completion and carefully weighed to determine a quantitative evaluation of the area. The results of this second deter-

mination are shown in Fig. 3.

The data from the second determination were interpreted as a regression line of the form $y = B_0 + B x$. Estimates of 4.0156 and .004972 were obtained by the method of least squares [6] for B_0 and B respectively. The length of the mercury, y, was a linear function of its location in the capillary, x. Average values for y and x respectively were: 4.1998 cm at 37.050 cm from the capillary index. The estimates of B_0 and B were later used in the same form in calculating the coefficients of expansion of the test samples used in evaluating the system.

This linear relationship may be used to estimate the length of the mercury at any point in the capillary for the calculation of the cross-sectional area. The area thus determined will have a high degree of accuracy; the 95% confidence intervals for the length of the mercury were 4.078 ± .006 at 12.5 cm and 4.326 ± .008 at 62.5 cm.

The volume of mercury used in this procedure was determined by weighing the mercury on an analytic balance with an accuracy of one part per thousand. The weight was .1581 grams and the volume was determined to be .01168 cm^3, where the density was constant at 13.534 grams per milliliter. [4]

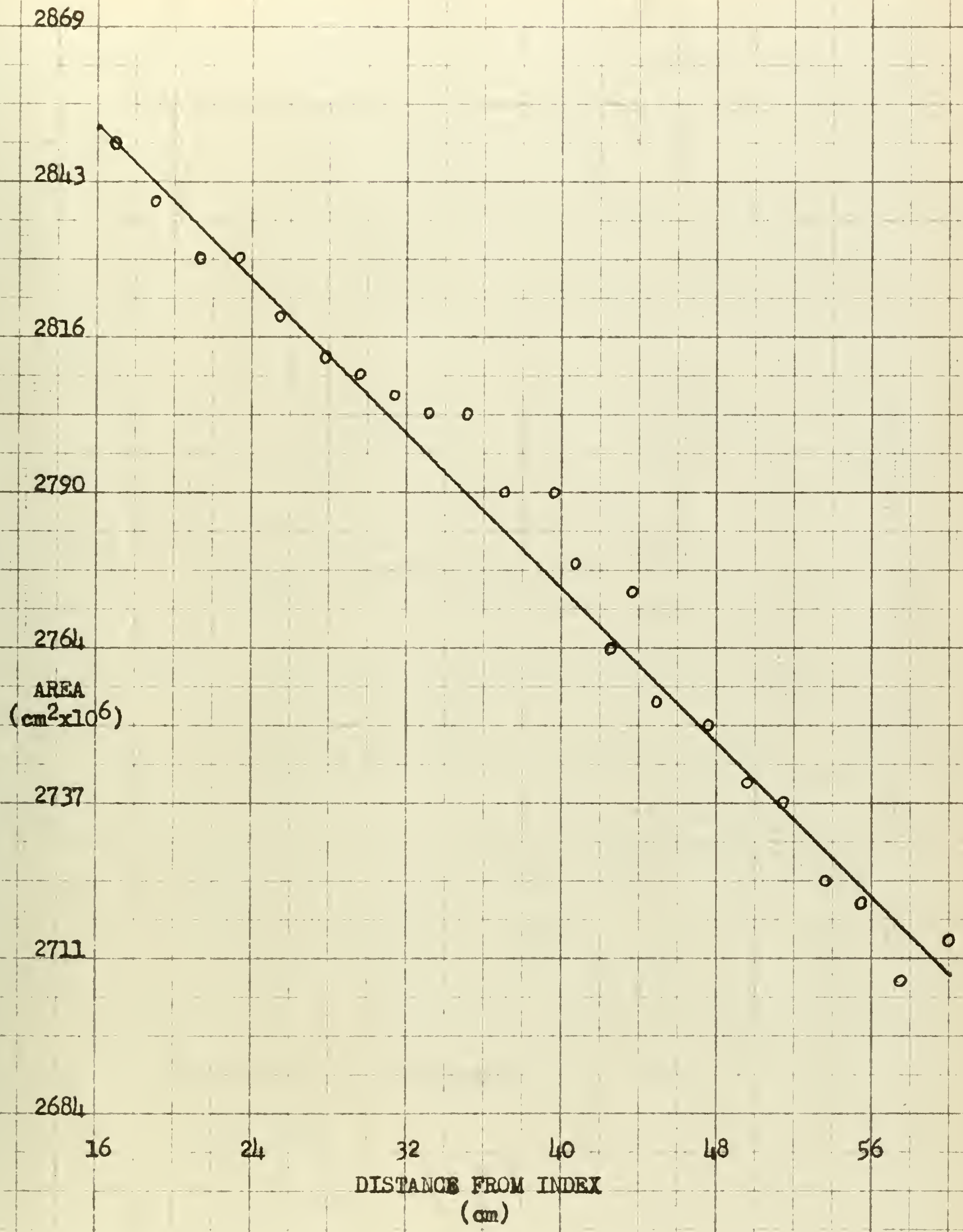

FIGURE 3 — Variation of Area in Capillary

APPENDIX III

TREATMENT OF DATA

The formula derived in Appendix I was not suitable for a statistical study in that the area was to be considered as varying as a function of the distance from the capillary index (Appendix II). It was necessary to assume that the coefficients of expansion would be essentially constant over the temperature range studied, and to rearrange the basic relationships into a form which would permit the problem to be handled as a regression.

The volume in the capillary as a function of distance, $V(x)$, had the following relationship to the volume of mercury, $V*$, used in determining the estimates of B_o and B (Appendix II).

$$V(x) = \int_0^x A(x)\,dx = \int_0^x \frac{V*}{B_o + B\,x}\,dx \qquad (1)$$

Integrating and evaluating at the initial conditions,

$$V(x) = \frac{V*}{B} \ln \left(1 + \frac{B}{B_o} x\right) \qquad (2)$$

The volume in the capillary as a function of temperature, $V(T)$, had the following relationship to the volume of the various components.

$$V(T) = V_m(T) + V_s(T) - V_g(T) = V(x)$$

$$V_s(T) = V(x) + V_g(T) - V_m(T)$$

$$\ln V_s(T) = \ln \left[V(x) + V_g(T) - V_m(T)\right] \qquad (3)$$

The volume of the individual components, V_i, are related to their coefficients of expansion and temperature by,

$$a_i = \frac{dV_i}{V_i\,dT}$$

Integrating and evaluating at the initial conditions, where T_1 is the initial temperature and equal to zero on a relative scale, and the

initial volume of the component is $V_{o,i}$

$$\ln V_i(T) = a_i\, T + \ln V_{o,i} \tag{4}$$

Combining equations (3) and (4) for the sample under test,

$$a_s\, T + \ln V_{o,s} = \ln \left[V(x) + V_g(T) - V_m(T) \right]$$

and rearranging to the final form.

$$a_s\, T = \ln \left\{ \frac{V(x) + Vg(T) - Vm(T)}{V_{o,s}} \right\} \tag{5}$$

In this form the problem reduces to a regression where T is the independent variable and the ln function the dependent variable. Fig. 4 is a graphical presentation of the data. Using the method of least squares [6] an estimate of a_s can be determined, and this in turn can be used with the various test statistics to evaluate the performance of the apparatus.

For the calibration exercise, using only mercury in the specimen bulb, it will be necessary to rearrange the above equation to

$$a_m\, T = \ln \left\{ \frac{V(x) + Vg(T)}{V_{o,m}} \right\} \tag{6}$$

In this exercise, the coefficient of expansion of the glass is assumed to be 1.00 x 10^{-5}/°C and the initial volume of the glass is assumed to be that of the specimen bulb. The values for V(x) and Vg(T) should be compiled for reference in that these same values will appear in all computations.

Having determined an estimate of a_s by the method of least squares, it is then possible to make the various significance tests [6] for determining confidence intervals and testing various hypotheses concerning the estimate of a_s.

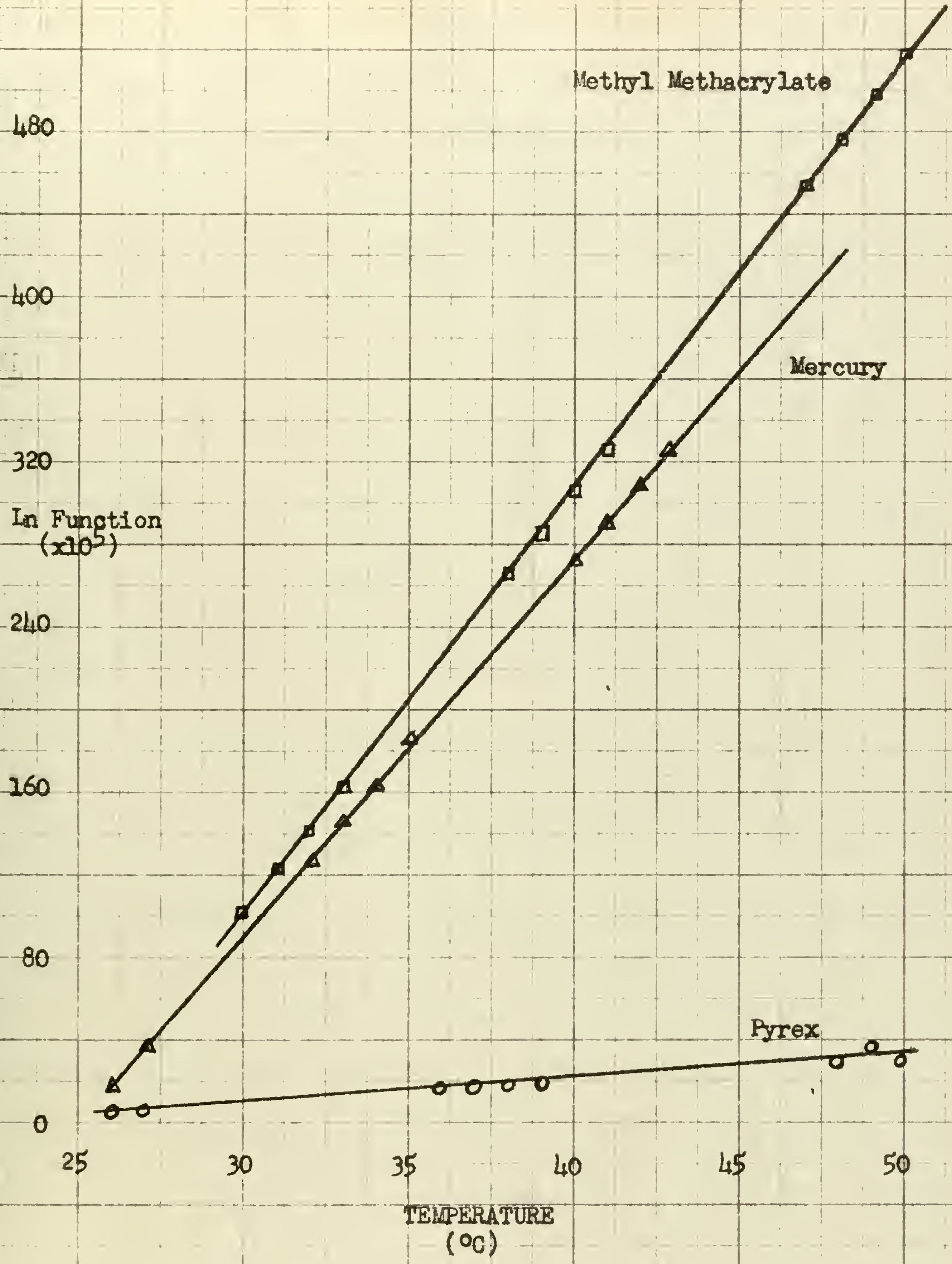

FIGURE 4 — Temperature-In Function for Typical Test Samples

The first test statistic was utilized to test the hypothesis that the estimate of a_m, the coefficient of expansion of the mercury, was equal to 18.194×10^{-5}, the accepted value for mercury [4]. Acceptance of the hypothesis implies that the apparatus is functioning correctly and that the assumptions concerning the glassware are significantly correct.

Another test statistic can be utilized to test the hypothesis that two estimates of a_s are equal. This will provide a measure of the reproducibility of the apparatus provided that there is good reason to believe that the coefficients of expansion should not change between any two runs due to effects other than the reproducibility of the apparatus. Such is the case of glass samples. This same test can be employed to determine if there is any significant difference due to conditions imposed on the sample--such as various conditioning periods or changes in composition.

The final operation to be conducted is the determination of the optimum sampling procedure. This will be possible only when the standard deviation of the ln function about the mean of $a_s T$ can be estimated with some confidence. On the completion of several hundred observations, this was estimated to be 2×10^{-5}. Using the applicable operating characteristics curve [6], a level of significance of five percent and a high probability of rejection when a_s differed by more than $.5 \times 10^{-5}$ /°C., the number of observations was found to be approximately 12. This requires a certain juggling of the temperatures at which the observations will be taken, but the optimum number of observations would appear to be at T equal to zero and three groups of four observations each, spaced one degree apart and grouped at the upper, lower and mean value of the temperature range.

It should be pointed out that this procedure is applicable to the dilatometer tested where the temperature range was 25°C, and the standard deviation was fairly well known from previous data. This sampling procedure was tested and proved entirely satisfactory.

APPENDIX IV

OPERATING INSTRUCTIONS

In general, the following instructions are the step-by-step procedure with special attention to those points which seemed to affect the accuracy or were responsible for difficulty in handling the mercury.

The glassware was cleaned very carefully, dried and closed off from the atmosphere when not in use. This is quite important, as any bubbles forming on the glassware will completely upset the accuracy of the equipment. This cleanliness must extend to the samples and the mercury as well. The samples used in the experiments were cleaned with soap and water, dried in an oven and handled with lint-free tissue paper thereafter. All mercury used in the tests had been distilled just beforehand.

With the sample in the specimen bulb, assemble the dilatometer and mercury reservoir for filling and place the system under vacuum up to the stop-cock of the reservoir. The dilatometer is then immersed in the temperature bath to a level just below the spherical ball and socket joint. This joint is sealed with De Khotinsky cement (to avoid overheating the specimen, melt the cement and transfer it with a spatula.) If the ball and socket joint has been fitted properly, this step is not necessary, but in the event of a leak, it will prevent the mercury from spilling into the bath. After smoothing out the De Khotinsky cement, place a laboratory C-clamp over the joint and tighten. Immerse the dilatometer to the bulb index and permit the system to fill with mercury. Insure that the specimen does not adhere to the side of the bulb leaving a vacant volume in the bulb. If the system is not vacuum tight, air bubbles will appear in the mercury-filling capillary section. This can usually be corrected by

tightening the spindle of the Kern-Exelo stop-cock. Permit the mercury to fill the bulb and capillary completely before securing the vacuum. With the vacuum removed and the temperature bath set at a selected level, allow the mercury to seek its own level; inspect the system carefully to insure that there are no bubbles on the glassware.

Set the cathetometer to the meniscus, taking observations every 15 minutes until there is no appreciable movement of the mercury in the capillary. Connect a small pressure bulb to the capillary and adjust the meniscus to the bulb index; close the mercury-filling stop-cock making sure that the channeled portion of the stop-cock is connected with the mercury reservoir. Continue the cathetometer observations of the meniscus, adjusting the level as necessary until satisfied that the system has reached equilibrium. This operation will take at least an hour or longer, depending largely on the specific heat of the sample. With the meniscus adjusted to the bulb index, remove the hose connection to the top of the capillary and replace with a small drying tube; this will prevent accumulation of moisture in the capillary. Remove the mercury reservoir by detaching it from the hose connection; manipulate the hose connection to remove as much excess mercury as possible.

Record the position of the capillary index and proceed with adjustment of the temperature and observation of the meniscus over the selected portion of the capillary. Allow sufficient time at each temperature for the system to each equilibrium. As a basis for estimate, 15 minutes was sufficient for a 1° C change. Inspect the water level at periodic intervals and keep it up to the bulb index.

A water bath was used for the tests; regulation will be adequate up

to 50° C, but beyond that point the meniscus will not settle out. Beyond 50° C the water bath will have to be replaced with oil or insulated sufficiently to decrease heat losses.

Once commenced, the determination must be carried through to completion without interruption. If the apparatus is permitted to cool and then reheated, it will require at least an additional 24 hours for the system to readjust to equilibrium.

The final step must be conducted with care or the entire run will be lost. This step is the volume determination of the sample. The volume of the sample at the end of the run will not be the same as it was at the start; it will not suffice to refill the specimen bulb with mercury should any be lost during the final step.

The dilatometer is removed from its supports and inverted. A finger placed over the capillary will prevent the mercury from changing position while the excess mercury in the filling connection is removed. Collection of the mercury from the capillary and specimen bulb can be accomplished by loosening the Kern-Exelo stop-cock slightly. When the bulb has drained, there will still be some mercury in the filling connection capillary. This can be removed by placing the dilatometer in its normal position and applying vacuum to the system, with the Kern-Exelo slightly loosened. When all the mercury has been drawn into the bulb proper, the spherical joint can be broken. If the glassware, specimen and sample were clean, all of the mercury can be removed easily. Do not reuse this mercury. Close and seal the system immediately after removing the specimen.

thesB8085
A dilatometer for determining the cubica
3 2768 002 08094 7
DUDLEY KNOX LIBRARY